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(72) Inventors: ERIK SVEND ERNST WERNER
JAN VERLOOP

(19)



(54) PROCESS FOR THE REMOVAL OF ACIDIC GASES

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organized under the laws of the Netherlands, of 30, Carel van Bylandtlaan, The Hague, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to a process for the removal of acidic gases from a gaseous mixture containing the same.

Processes for the removal of acidic gases, such as H₂S and CO₂, from gaseous mixtures containing the same are well known in the art. In general, these processes involve scrubbing the gaseous mixture with a liquid absorbent in an absorption zone whereby the acidic gases are removed from the gaseous mixture and a loaded absorbent stream (generally called the fat absorbent) is obtained which is passed to a regeneration zone where the absorbent is heated and/or stripped with solvent vapour, e.g., steam, resulting in the release of the acidic gases. The regenerated absorbent (generally called the lean absorbent) is returned into contact with the feed gas mixture in the absorption zone while the evolved acidic gases are passed to a cooler/condenser in which the solvent vapours are condensed and separated from the acidic gases.

For a variety of industrial applications, it is further necessary or desirable to reduce the sulphur content of a gaseous mixture containing significant quantities of COS and/or mercaptans in addition to H₂S and CO₂ to low levels prior to further processing and/or utilization of the gaseous mixture. For example, sour gas available from certain natural gas reservoirs is known to contain up to about 0.1% by volume (1000 ppm) COS and some 0.01% by volume (100 ppm) mercaptans in addition to substantial quantities of H₂S and CO₂. Since the COS and mercaptans present in the sour gas make-up part of the total sulphur, substantial removal of same, in addition to the H₂S present, is necessary to meet many of the specifications for conventional end uses of such gas, e.g., residential heating and industrial uses. Further, in conventional partial combustion process utilizing sour liquid hydrocarbon oils or sulphur-containing coals as the primary fuel source, a crude synthesis gas product is obtained which typically contains 100 to 1500 ppm COS in addition to the H₂S and CO₂ partial combustion by-products. In many cases this crude synthesis gas product is subject to further processing, e.g., contact with sulphur-sensitive CO-shift catalysts in hydrogen manufacture, or funnelled to industrial and consumer end-uses, e.g., as energy source in gas turbine generation of electricity or as a town gas for private consumption, which makes it desirable or even essential that the total sulphur content of the combustion gas be reduced to very low levels.

Although the commercially available gas-treating processes are generally satisfactory with respect to the degree of removal of undesirable gas contaminants, there is still room for further improvement of such processes. A major cost factor for these regenerative processes constitutes the stripping steam requirement for regenerating the fat absorbent which can be very high for many solvents. The said steam requirement is greatly dependent

on the amount of absorbent circulating, so that reduction of this absorbent circulation would necessarily bring about a reduction in the steam consumption. The amount of absorbent to be used in a particular case is dictated by the partial pressures of the acidic gas components in the gaseous mixture to be treated and the desired degree of gas purification. A reduction in the absorbent circulation would also contribute to further savings from a capital cost point of view in that smaller absorption and regeneration columns are required and in that less absorbent solvent for filling the columns is necessary.

It is an object of the invention to provide a process for the removal of acidic gases as identified to a very high degree while using a reduced absorbent circulation.

Accordingly, the present invention relates to a process for the removal of acidic gases from a gaseous mixture containing the same in which the said gaseous mixture is countercurrently contacted in a contacting zone at a temperature in the range of 15 to 135°C and a pressure in the range of 1 to 100 kg 1cm 2abs. with an aqueous absorbent comprising an amine with a pK_b of 3-14 at 25°C in an amount of 10 to 70% by weight and sulfolane and/or its derivatives in an amount of 25 to 70% by weight, which aqueous absorbent is introduced at the top of the contacting zone, and at a point between the middle and the bottom of said zone withdrawn therefrom as a semi-fat absorbent and reintroduced at a point of said zone which is lower than the point from which it has been withdrawn after having externally been cooled, for further contacting of the said gaseous mixture, whereafter a fat aqueous absorbent is finally withdrawn from the bottom of the contacting zone and regenerated by means of heating and/or stripping at a pressure of 0.0-4 kg/cm² gauge.

The process of the present invention is particularly suitable for treating gaseous mixtures comprising acidic gases at relatively low partial pressures. This may be the case when the mixture to be treated comprises little acidic gas components or when it contains the said gas components at relatively low pressures. The sum of the partial pressures of hydrogen sulphide and carbon dioxide should preferably be lower than 3.0 bar abs., and more preferably lower than 2.0 bar abs. at the temperature applied during absorption. The greatest benefit will be derived from the process of the invention when applying it to gaseous mixtures having a hydrogen sulphide partial pressure in the range of from 0.025 to 0.6 bar abs. at a lean absorbent temperature of 30° to 65°C. In applying the process of the invention for the removal of carbon dioxide from gaseous mixtures comprising substantially no hydrogen sulphide (less than 0.1% vol. H₂S) the carbon dioxide partial pressures may vary in the range of from 0.1 to 2.0 bar abs. at a lean absorbent temperature as indicated.

The process of the invention is also very suitable for application in those areas of the world where deep cooling to temperatures below 50°C is not well possible because the ambient temperature in these areas during at least part of the year does not drop below the figure indicated. Even in these instances intermediate cooling to temperatures of about 65°C may considerably add to reducing the absorbent circulation.

The contacting zone used preferably comprises of from 10 to 50 contacting layers, such as valve trays, bubble cap trays, baffles and the like. The aqueous absorbent is suitably withdrawn at point above the second contacting layer but below the fifteenth contacting layer of the absorption zone if 20 layers or more are applied or below the tenth contacting layer if less than 20 layers are applied.

The aqueous absorbent used in the present process comprises a "chemical" solvent part, i.e., one or more amines and a "physical" solvent part, i.e., sulfolane and/or its derivatives.

For the process according to the invention the said amines should have a weakly basic character. (The basic strength of a compound is conveniently expressed in terms of the negative logarithm of the basic dissociation constant. Thus, a strong base has a low pK_b , while a weak base has a value approaching the upper limit $pK_b = 14$). Bases suitable for the process according to the invention has a pK_b at 25°C in the range of 3 to 14. Alkanolamines are particularly suitable, especially those amines having 1 to 4, and preferably 2 or 3, carbon atoms per alkanol radical. Typical species are, inter alia, monoethanol-amine, diethanolamine, methyldiethanolamine, diisopropanolamine, triethanolamine and mixture thereof. Especially the dialkanolamines can be used with advantage.

The physical solvent part comprises certain components or mixtures thereof, selected from the group of cyclotetramethylene sulphones. The derivatives from the basic sulphone cyclotetramethylene sulphone (thiophene tetrahydro-1,1-dioxide) which is also known as sulfolane, should preferably have not more than 4, more preferably not more than 2 alkyl substituents in the tetramethylene sulphone ring. Sulfolane itself is the preferred species of this class of compounds.

It has been found advantageous to use in the process an aqueous absorbent which preferably contains the amine(s) within the range of 20-55%wt. An absorbent containing 30-45%wt of the amine(s) has been found very suitable. The sulfolane or its derivatives are preferably present in the absorbent in an amount of 30 to 55%wt. The balance of the mixed

solvent consists essentially of water, generally in the range of 5-35%wt.

The descending aqueous absorbent can be withdrawn from the absorption column by means of a total draw-off tray. Such a tray divides the column in two sections with respect to the flow of absorbent, but has a passage for the rising gas mixture to allow it to pass from the lower section into the upper section. The absorbent collected on the draw-off tray is withdrawn from the absorption column and externally cooled preferably by indirect heat exchange to a temperature in the range of from 20 to 70°C. More preferably, the withdrawn aqueous absorbent which is semi-fat, is cooled to a temperature which is the same as the temperature of the aqueous absorbent introduced at the top of the absorption column. Thereafter the cooled, semi-fat absorbent is reintroduced into the column in the lower section, preferably directly under the total draw-off tray. It will be evident by the position of the total draw-off tray that the lower section of the column is shorter than the upper section of the column, which latter section encompasses more absorption trays.

It is also possible to use as contacting zone two absorption columns of different column length and arranged such that the gaseous mixture contacts first in the shorter one of the two columns a cooled semi-fat absorbent introduced at the top of this shorter column and then countercurrently contacts a lean absorbent in the taller one of the two columns. The fat absorbent leaving the shorter column is regenerated, cooled and introduced at the top of the taller column as the lean absorbent.

The principal attainment of the process of this invention is the high degree of removal of acidic gas components from gaseous mixtures at very low partial pressures of these acidic gas components and at reduced absorbent flows. Because a low temperature has a particularly favourable effect on the absorption of hydrogen sulphide and/or carbon dioxide, intermediate cooling of the absorbent before its introduction into the lower section results in more favourable absorption equilibria for hydrogen sulphide and/or carbon dioxide in the bottom of the absorption column. When a gaseous mixture enters the lower section of the absorption column countercurrent to a descending stream of cold liquid absorbent, a high degree of absorption is obtained even at the relatively low partial pressures of the acidic gases. This high degree of absorption is maintained as the total amount of acidic gas components progressively decreases as the gas mixture proceeds upward in the column, because in proceeding upwards the gaseous mixture is contacted with an absorbent, the temperature whereof is decreasing.

Gaseous mixtures which can advantageously be treated by the process according to the invention, include natural gas, refinery gas or synthesis gas obtained by the partial oxidation of heavy oil fractions or coal. The process is particularly attractive for the treatment of gases containing high amounts of acidic gases, such as hydrogen sulphide and carbon dioxide at relatively low partial pressures. The gaseous mixtures to be treated in accordance with the process of the present invention may also contain carbonyl sulphide in amounts of from 0 to 1500 ppmv and mercaptans in amounts of from 0 to 500 ppmv. The process may be adapted to treat such feedstocks which also contain higher molecular weight hydrocarbons.

An important step in the process of the invention comprises intimately contacting the gaseous mixture and the aqueous absorbent at pressures in the range of 1 to 100 kg/cm² abs. A preferred pressure range is from 5 to 70 kg/cm² abs. A highly preferred aspect of the operation of the absorption column is to conduct absorption under countercurrent contacting at temperatures in the range of about 15°C to 135°C, more preferably of 30°C to 80°C and wherein the temperature of the bottom of the absorption tower is 5°C to 30°C higher than the temperature in the top part of the absorption zone. Normally, intimate contacting is effected in a vertical column, the sweet dry gas leaving the column near or at the top while the fat absorbent solution leaves at or near the bottom of this column.

The fat absorbent contains dissolved acidic gases, such as hydrogen sulphide and carbon dioxide, carbonyl sulphide and/or mercaptans, together with possible contaminating proportions of hydrocarbons, originally present in the gaseous mixture. Under the preferred absorption conditions, the proportion of hydrocarbons contaminant to hydrogen sulphide is maintained at a low level.

The fat absorbent is preferably conducted from the bottom portion of the absorption column under high pressure to a regeneration zone wherein the pressure is reduced to 0.0-4 kg/cm² gauge for the purpose of removing the acidic gases and other absorbed gaseous contaminants. In this zone, referred to as a gas stripper or stripper column, the solution is heated to a temperature sufficient to volatilize the acidic gases and other absorbed gaseous contaminants, and water therefrom, which leave the stripping column at the top. The fat absorbent may also be sent firstly to a flashing zone wherein a major part of the absorbed acidic gases and other absorbed gaseous contaminants is removed from the absorbent by reducing the pressure to 1.5-8 kg/cm² abs. Thereafter the absorbent is regenerated as described.

One of the chief advantages of the use of the aqueous absorbent of the present invention is experienced during the stripping operation.

It has been found that in stripping the fat absorbent to remove the acidic gases absorbed the steam requirement per unit volume of absorbent is more or less constant. Thus, by reducing the solvent circulation less steam has to be used. It is possible to employ stripping temperatures between about 100°C and 190°C at pressures between about 0 and 4 kg/cm² gauge. The use of these low regeneration temperatures has a distinct advantage in that any thermal degradation of the organic solvent fractions of the absorbent is greatly reduced. In the drawings accompanying the Provisional specification,

Figure 1 shows a schematic flow diagram of an embodiment of the process of the invention, in which a gaseous feed stream is countercurrently contacted with a descending absorbent flow. Apart from the heat exchangers and pumps shown any further ancillary equipment has been omitted.

Figure 2 shows a different embodiment of the process of the invention in which two separate absorption columns are used instead of a single column divided into two separate sections.

In Figure 1 a gaseous mixture comprising acidic gases is introduced into the lower section of an absorption column 2 via a line 1. The absorption column 2 is provided with trays of which the lowest one is indicated by *a* and the top one by *b*. The said column is divided in two sections by means of a total draw-off tray 4 which is provided somewhere between the second and tenth tray. The gaseous mixture is introduced below the first tray (tray *a*) and the aqueous absorbent is introduced above the top tray (tray *b*) via a line 9. The gaseous mixture rises in the lower section and passes via the total draw-off tray 4 into the upper section of the column. It is counter-currently contacted by the descending aqueous absorbent. As a result of the released heat of absorption during the absorption of acidic gases the aqueous absorbent is gradually increasing in temperature. The warmed-up absorbent is withdrawn from the column via a line 5 and externally cooled in a heat exchanger 6 and re-introduced into the lower section of the absorption column 2 by means of a pump 7 and a line 8. The gaseous mixture in the lower section is contacted with a cooled and semi-fat aqueous absorbent. As a result of the absorption of the acidic gases the temperature of the absorbent rises again.

The treated gaseous mixture which is now substantially free of acidic gases and/or carbonyl sulphide and/or mercaptans, if present, leaves the column via a line 11. The hot, fat absorbent leaves the column 2 at the bottom thereof via a line 12 and is heat-exchanged with hot, regenerated absorbent in a heat exchanger 10. Thereafter, the fat aqueous absorbent is introduced into a stripper column 13 for regeneration.

The stripper column operates at a reduced pressure with respect to the pressure applied in the absorption column. It is heated by means of a reboiler 18. Hot aqueous absorbent is withdrawn at the bottom of the stripper column 13 via a line 14 and further heated in the reboiler 18. It is re-introduced into the stripper column via a line 19. The acidic gases stripped from the absorbent leave the stripper column via a line 20. The lean regenerated absorbent leaves the stripper column 13 via a line 15 and is pumped back to the absorption column 2 by means of a pump 16. The hot lean absorbent is cooled by heat exchange in the heat exchanger 10 as set out above and further cooled in a cooler 17.

The acidic gases obtained in the process of the invention can be used for the preparation of elemental sulphur. This may be done by the well-known modified Claus process. Depending on the H₂S/CO₂ ratio in the acidic gases they may be fed directly - preferably after cooling and condensation of the water vapour - into the thermal stage of the sulphur recovery unit or they should be subjected to a further enrichment step prior to their introduction into the said thermal stage.

In Figure 2 the same reference numerals have been used for identical parts. Instead of a single column 2 two separate columns 2*a* and 2*b* are used. The gaseous mixture leaves column 2*a* - comparable with the lower section of the column 2 in Figure 1 - via a line 40 at the top and enters column 2*b* at the bottom thereof. The semi-fat absorbent leaves column 2*b* at its bottom and is introduced after cooling at the top of column 2*a*.

The invention will now be illustrated with the following Examples.

Example 1

A natural gas feed system comprising 3 vol.% H₂S and 12 vol.% CO₂ was fed at a temperature of 40°C and a pressure of 12 bar abs. and a flow rate of 100,000 Nm³/h to an absorber/stripper unit as shown in Figure 1. The aqueous absorbent used comprised 45% of di-isopropanolamine, 40% of sulfolane and 15% by weight of water. It was introduced at the top of the absorber column at a temperature of 41°C. The column was provided with 40 trays, a total draw-off tray being installed between the 3rd and 4th tray. The temperature of the semi-fat absorbent withdrawn from the column was 66°C. The absorbent was externally

cooled with water and reintroduced at a temperature of 41°C directly under the draw-off tray. The temperature of the fat absorbent leaving the column was 57°C and passed at indirect heat exchange with the hot, lean absorbent to the regeneration column. It was introduced at a temperature of 91°C into the regeneration column operating at a pressure of 2.0 kg/cm² abs. The regenerated lean absorbent left the regeneration column at a temperature of 137°C. After heat exchange with the fat absorbent and cooling with water it was introduced at a temperature of 41°C at the top of the absorber column.

The treated gas mixture leaving at the top of the absorber column comprised less than 4 ppm H₂S and 500 ppm CO₂.

The amount of absorbent flow was 360 m³/h and the amount of steam required for the regeneration 43 tons/h.

Processing of the above feed in a standard gas treating unit not having external cooling facilities as shown in the Figure and having 35 trays, would have required 500 m³/h of absorbent and 57 tons/h of steam to obtain the same degree of purification of the gaseous mixture treated.

Example II

In the same manner as described in Example I two further experiments were carried out with feed gases of different compositions and at different flow rates. The reaction conditions and the results obtained have been tabulated in the Table. In this Table also the conditions and results of the experiment of Example I have been inserted as Experiment No. 1.

TABLE

Experiment	1		2		3	
Intermediate cooling	no	yes	no	yes	no	yes
Total pressure, bara	12	12	13	13	17	17
<i>Feed gas</i>						
flow, Nm^3/h	100.000	100.000	200.000	200.000	35.000	35.000
composition, %v						
H ₂ S	3	3	0.7	0.7	7.1	7.1
CO ₂	12	12	2.5	2.5	9.1	9.1
others	85	85	96.8	96.8	83.8	83.8
<i>Treated gas</i>						
composition, %v						
H ₂ S	<0.0004	<0.0004	<0.0010	<0.0010	0.0500	0.0500
CO ₂	0.050	0.050	0.200	0.200	0.6500	1.70
others	rest	rest	rest	rest	rest	rest
solvent flow, m^3/h	500	360	260	185	200	160
Solvent composition, %w						
Di-isopropanolamine	45	45	45	45	45	45
Sulfolane	40	40	40	40	37	37
Water	15	15	15	15	18	18

Experiment	1	2	3
<i>Temperatures, °C</i>			
Lean absorbent to absorber	41	35	40
Semi-fat absorbent to intermediate cooler	-	55	55
Semi-fat absorbent ex intermediate cooler	41	35	42
Fat absorbent ex absorber	74	53	60
Number of absorber trays	35	20 ^b	10 ^c
Steam consumption, tons/h	57	18	14.5

Notes: 1. In experiments 1 and 3 the other components of the feed gas were mainly hydrocarbons; in experiment 2 the others comprised N₂, N₂, CO and H₂O.
 2. *a* the semi-fat solvent was drawn off between the 3rd and 4th tray;
b ditto between the 3rd and 4th tray;
c ditto between the 3rd and 4th tray.

WHAT WE CLAIM IS:

1. A process for the removal of acidic gases from a gaseous mixture containing the same in which the said gaseous mixture is countercurrently contacted in a contacting zone at a temperature in the range of 15 to 135°C and a pressure in the range of 1 to 100 kg/cm² abs with an aqueous absorbent comprising an amine with a pK_b of 3-14 at 25°C in an amount of 10 to 70% by weight and sulfolane and/or its derivatives in an amount of 25 to 70% by weight, which aqueous absorbent is introduced at the top of the contacting zone, and at a point between the middle and the bottom of the said zone withdrawn therefrom as a semi-fat absorbent and re-introduced at a point of said zone which is lower than the point from which it has been withdrawn after having externally been cooled, for further contacting of said gaseous mixture, whereafter a fat aqueous absorbent is finally withdrawn from the contacting zone at the bottom thereof and regenerated by means of heating and/or stripping at a pressure of 0.0-4 kg/cm² gauge.
2. A process as claimed in claim 1, in which the contacting zone comprises of from 10 to 50 contacting layers and wherein the aqueous absorbent is withdrawn at a point above the second contacting layer.
3. A process as claimed in claim 2, in which the contacting zone comprises 20 or more contacting layers and wherein the aqueous absorbent is withdrawn at a point below the fifteenth contacting layer.
4. A process as claimed in claim 2, in which the contacting zone comprises less than 20 layers and wherein the aqueous absorbent is withdrawn at a point below the tenth contacting layer.
5. A process as claimed in any one of claims 1 to 4, in which the withdrawn aqueous absorbent is externally cooled to a temperature in the range of from 10 to 70°C.
6. A process as claimed in any one of claims 1 to 5, in which the withdrawn absorbent is externally cooled to a temperature which is the same or substantially the same as the temperature of the aqueous absorbent introduced at the top of the absorption column.
7. A process as claimed in any one of claims 1 to 6, in which the absorption zone is divided in an upper section and a lower section with respect to the flow of the said absorbent by a total draw-off layer for the absorbent.
8. A process as claimed in any one of claims 1 to 6, in which the absorption zone comprises two absorption columns of different column length and arranged such that the gaseous mixture contacts first in the shorter one of the two columns a cooled, semi-fat absorbent introduced at the top of this shorter column and then countercurrently contacts a lean absorbent in the taller one of the two columns, the fat absorbent leaving the shorter column being regenerated, cooled, and introduced at the top of the taller column as the lean absorbent.
9. A process as claimed in claim 7, in which the cooled, semi-fat absorbent is introduced in the lower section directly below the said total draw-off layer.
10. A process as claimed in any one of claims 1 to 9, in which the gaseous mixture comprises hydrogen sulphide and carbon dioxide at such partial pressures that the sum thereof is lower than 3.0 bar abs. at the temperature applied during absorption.
11. A process as claimed in any one of claims 1 to 10, in which the gaseous mixture comprises hydrogen sulphide at a partial pressure in the range of from 0.025 to 0.6 bar abs. at a lean absorbent temperature of 30 to 65°C.
12. A process as claimed in any one of claims 1 to 9, in which the gaseous mixture is substantially free of hydrogen sulphide and comprises carbon dioxide at a partial pressure in the range of from 0.1 to 2.0 bar abs. at a lean absorbent temperature of 30 to 65°C.
13. A process as claimed in any one of claims 1 to 12, in which the gaseous mixture is contacted with the aqueous absorbent at a pressure in the range of from 5 to 70 kg/cm² abs.
14. A process as claimed in any one of claims 1 to 13, in which the amine is di-isopropanolamine or methyl diethanolamine.
15. A process as claimed in any one of claims 1 to 14, in which the fat aqueous absorbent is regenerated at a temperature in the range of from 100 to 190°C.
16. A process as claimed in claim 1, substantially as hereinbefore described with special reference to the drawings accompanying the provisional specification and the Examples.

R.C. ROGERS,
Chartered Patent Agent,
Shell Centre,
London, S.E.1 7NA.
Agent for the Applicants.

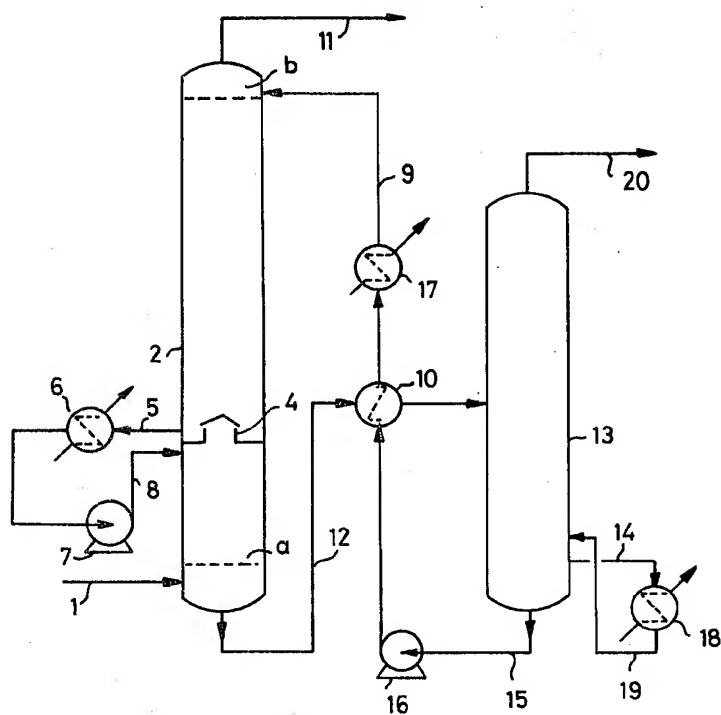


FIG. 1

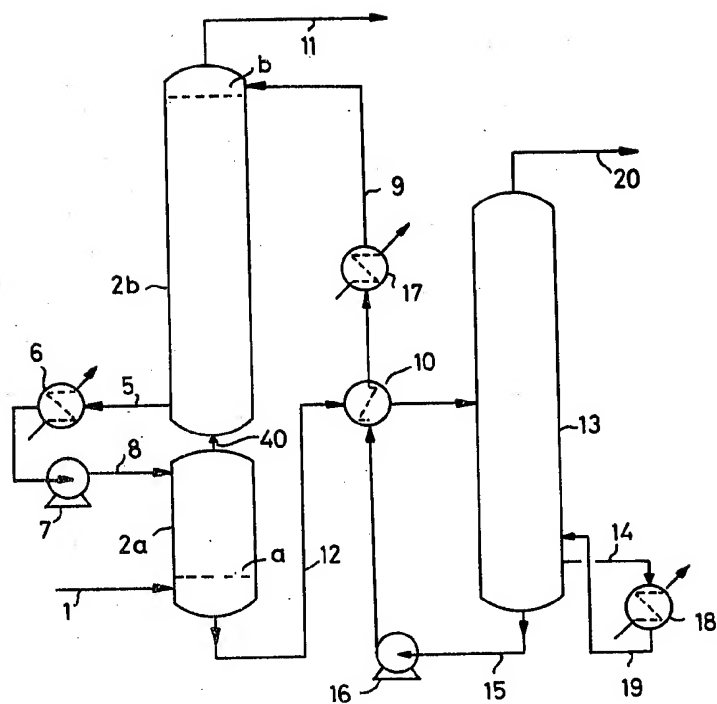


FIG. 2